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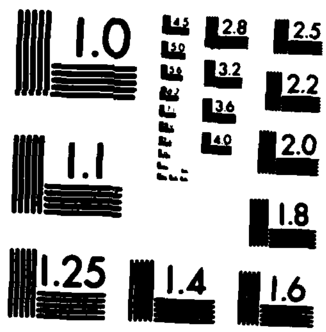

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"Research on Submicrometer Structures"

Final Report

covering the period
1 August 1979 to 31 July 1984

Contract N00014-79-C-0908

Prepared for:

Defense Advanced Research Projects Agency

by:

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Abstract

Research under this contract was conducted in two phases. In phase 1, ~~(1 August 1979 - 31 July 1982)~~ the objective was to establish a submicrometer structures research lab on the MIT campus, to develop fabrication techniques for the spatial domain below 1000Å, and to pursue several areas of interdisciplinary research. Research under phase 1 saw the development of an effective sub-1000Å technology, successful alignment of liquid crystal films, progress in our understanding of the graphoepitaxy phenomenon, and attachment of organic molecules to submicrometer structures. In phase 2, ~~(1 August 1982 -~~ 31 July 1984) we demonstrated surface-energy-driven secondary grain growth in Si and Ge and showed that graphoepitaxial alignment of Ge can be achieved using this grain growth process. These results indicate that if the temperature required for secondary grain growth can be driven down then graphoepitaxy should be able to form the basis of a general process for obtaining single-crystal device films, of virtually any material, on amorphous substrates. This would have significant impact on future military systems.

I. Introduction

This contract was established in August 1979. It's initial objective (phase 1) was to help establish submicrometer-structures research on the M.I.T. campus and to stimulate interdisciplinary applications of submicrometer structures. The DARPA support was crucial in creating at M.I.T. a broad research capability in submicrometer structures and stimulating interdisciplinary research. Accomplishments under phase 1 of this contract are summarized in Section IV.A., and publications under phase 1 are listed in Section V.A.

In August 1982 the contract was renewed for 2 years and focused on graphoepitaxy research. We refer to this period as phase 2 of the contract. Accomplishments under phase 2 are summarized in Section IV.B., and major publications are listed in Section V.B.

II. Impact of Graphoepitaxy on Military Systems

In the 1990's and beyond, military systems will require the integration, on the same substrate, of electronic, optical, acoustic and IR sensor devices in complex configurations, sometimes with vertical layering or 3D integration. Conventional techniques for growing single-crystal thin films, such as CVD, LPCVD, MOCVD and MBE cannot, by themselves, meet all future materials needs because they require single-crystal substrates with matching or near-matching lattice parameters. Techniques based on zone-melting recrystallization have produced device-quality Si films on amorphous substrates, and may soon yield device-quality Ge films on amorphous substrates, which could serve as substrates for GaAs eptiaxial growth. However, because the Si (or Ge) is melted and resolidified, high temperatures are used. This militates against 3D integration and imposes a number of additional constraints.

Under phase 2 of this contract we proposed to investigate two approaches to the formation of single-crystal films of Si, GaAs and other compound semiconductors on insulating amorphous substrates. Both were based on the use of a submicrometer-period artificial surface-relief template to induce orientation (i.e., graphoepitaxy). Thus, they held promise of circumventing the major shortcoming of conventional crystal growth techniques: dependence on a single-crystal substrate. They also would circumvent the major shortcoming of zone-melting recrystallization techniques: the need to melt the starting material. The two approaches were: 1) Si graphoepitaxy by SiI_4 CVD, and 2) surface-energy-driven graphoepitaxy. The first had been pursued as one task in phase 1 of this contract. The second was a completely novel approach to fabricating ultrathin single-crystal films on amorphous substrates which should be applicable to the full spectrum of device materials. If one could produce single-crystal ultrathin films on an amorphous substrate by surface-energy-driven graphoepitaxy then thicker crystalline films or heterostructures, as required for devices, could subsequently be grown over the ultrathin films by conventional low-temperature deposition processes (e.g., CVD, LPCVD, MOCVD, MBE).

III. Objectives of Research Contract

A. Phase 1 Objectives

Under phase 1 we proposed to conduct research in four areas:

1. fundamental limitations of microfabrication;
2. submicrometer structures and liquid crystal research;
3. graphoepitaxy;
4. attachment and properties of organic molecules on submicrometer structures.

A major objective of this program was to stimulate interdisciplinary research involving several academic departments.

B. Phase 2 Objectives

Under phase 2 we proposed a two-year program of research and development to adapt graphoepitaxy to the fabrication of single-crystal films for devices. The long-range goal was to provide a technology able to meet the demands of future DoD device systems for the integration of several different materials on the same substrates and for 3D integration. The intention was to work initially with Si and two distinct processes, surface-energy-driven graphoepitaxy and SiI_4 CVD, and if we were successful with the Si, to move on to other materials such as GaAs and HgCdTe. The items of the Work Statement were as follows:

1. Investigate the feasibility of surface-energy-driven graphoepitaxy for providing thin single-crystal films of Si, GaAs and other compound semiconductors on insulating, amorphous substrates;

2. Investigate the feasibility of achieving single-crystal films of Si by graphoepitaxy using the SiI_4 CVD process.

3. Develop the technology of graphoepitaxy, including methods of relief structure fabrication, with a view to providing means for integrating several device films on the same substrate and three-dimensional devices.

IV. Accomplishments Under Research Contract

A. Phase 1 of Contract

With DARPA support, as well as support from other sponsors, we established a laboratory at M.I.T. with unique capabilities for fabricating

submicrometer structures, and successfully pursued research in several interdisciplinary areas.

We investigated the techniques of holographic and x-ray lithography, and spatial-period division, and pushed linewidths well below 1000Å. A shadowing technique was used to fabricate x-ray masks with linewidths of 300Å, and this mask was successfully replicated. Reactive-ion etching, electroplating and liftoff were also developed and successfully used to produce useful structures of 2000Å period with linewidths down to 300Å. These results are described in publications listed in Section V.A.

Several liquid crystals were uniformly aligned using 3000Å and 2000Å-period gratings produced in quartz by holographic lithography and reactive-ion etching. This permitted a number of basic studies of liquid crystal physics to be carried out, as described in two publications listed in Section V.A. (H. von Kanel as first author).

The mechanism responsible for the orientation observed when Si is recrystallized over surface-relief gratings was investigated. We determined that the orientation occurs in a partially-molten transition region, most probably during solid-state grain growth just below the melting point. We also investigated graphoepitaxy from solution and determined that the effect is quite strong in alkali halides but the method is not adaptable to, or practical for, semiconductor films. Publications are listed in Section V.A.

We investigated a number of means for attachment of organic molecules to submicron structures. The most successful involved silane chemistry. For example, amino silane molecules were attached to an aluminum surface in a patterned monolayer. This pattern was then built up to a crosslinked network by several alternating immersions in a bifunctinal epoxide and a diamine.

B. <u>Phase 2 of Contract</u>

We demonstrated that the phenomenon of surface-energy-driven secondary grain growth does indeed occur, as we had predicted, in ultrathin (~300Å) films of Si and Ge, and that the dependences on film thickness, temperature and doping were also in reasonable accord with theory. However, the dependence on time deviated strongly from predictions: grain growth occurs rapidly at first but slows down abruptly after only a few minutes. All indications are that this phenomenon should be applicable to nearly any material.

In the case of Ge over surface-relief gratings in SiO_2 we demonstrated that graphoepitaxy does indeed occur by a purely solid state, surface-energy-driven grain-growth process. We consider this a highly significant achievement which opens the door to new means for preparing device films without the constraint of lattice matching to a substrate. Our results on Si and Ge are given in publications listed in Section V.B. Future goals of the surface-energy-driven graphoepitaxy research will be to develop means for driving down the temperature required to achieve orientation, and to improve the overall quality of films.

We also investigated the use of SiI_4 CVD to achieve graphoepitaxy. This was the subject of a Ph.D. thesis (S. Dana). We found that a grating could induce preferential nucleation but, because deposition conditions were far from equilibrium, alignment could not be achieved. A series of experiments were carried out in an oscillatory, single-zone furnace. This approach was abandoned when we determined that we could not restrict growth to the substrate plane. Instead, crystallites preferred to grow in a direction normal to the surface.

V. Listing of Publications Under the Contract

A. Phase 1

Journal Articles

M.W. Geis, D.A. Antoniadis, D.J. Silversmith, R.W. Mountain and H.I. Smith, "Silicon Graphoepitaxy using a Strip-Heater Oven", Appl. Phys. Lett. 37, 454 (1980).

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A.M. Hawryluk, N.M. Ceglio, R.H. Price, J. Melngailis and H.I. Smith, "Gold Transmission Gratings with Submicrometer Periods and Thicknesses $>0.5\mu m$", J. Vac. Sci. Technol. 19, 897 (1981).

N. Tsumita, J. Melngailis, A.M. Hawryluk and H.I. Smith, "Fabrication of X-Ray Masks Using Anisotropic Etching of (110) Si and Shadowing Techniques", J. Vac. Sci. Technol. 19, 1211 (1981).

N.N. Efremow, N.P. Economou, K. Bezjian, S.S. Dana and H.I. Smith, "A Simple Technique for Modifying the Profile of Resist Exposed by Holographic Lithography", J. Vac. Sci. Technol. 19, 1234 (1981).

C.M. Horwitz and J. Melngailis, "Reactive Sputter Etching of Si, SiO_2, Cr, and Other Materials with Gas Mixtures Based on CF_4 and Cl_2", J. Vac. Sci. Technol. 19, 1408 (1981).

K.A. Bezjian, H.I. Smith, J.M. Carter and M.W. Geis, "An Etch Pit Technique for Analyzing Crystallographic Orientation in Si Films", J. Electrochem. Soc. 129, 1848 (1982).

H.I. Smith, C.V. Thompson, M.W. Geis, R.A. Lemons and M.A. Bosch, "The Mechanism of Orientation in Si Graphoepitaxy by Laser or Strip-Heater Recrystallization", J. Electrochem. Soc., 130, 2050 (1983).

Theses

A.M. Hawryluk, "Transmission Diffraction Gratings for Soft X-Ray Spectroscopy and Spatial Period Division", Ph.D. Thesis, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, October 1981. (Also VLSI Memo 81-69, M.I.T., October 1981.)

B. Phase 2

Journal Articles

H.I. Smith, M.W. Geis, C.V. Thompson and H.A. Atwater, "Silicon-on-Insulator by Graphoepitaxy and Zone-Melting Recrystallization of Patterned Films", J. Crystal Growth, 63, 527 (1983).

E.H. Anderson, C.M. Horwitz and H. I. Smith, "Holographic Lithography With Thick Photoresist", Appl. Phys. Lett., 42, 874 (1983).

A.M. Hawryluk, H. I. Smith and D.J. Ehrlich, "Deep UV Spatial-Frequency Doubling by Combining Multilayer Mirrors with Diffraction Gratings", J. Vac. Sci. Technol. B, 1, 1200 (1983).

H.J. Lezec, E.H. Anderson and H. I. Smith, "An Improved Technique for Resist-Profile Control in Holographic Lithography", J. Vac. Sci. Technol. B, 1, 1204 (1983).

Henry I. Smith, C.V. Thompson and H.A. Atwater, "Graphoepitaxy and Zone-Melting Recrystallization of Patterned Films", J. Cryst. Growth, 65, 337 (1983).

C.V. Thompson and H.I. Smith, "Surface-Energy-Driven Secondary Grain Growth in Ultrathin (<100 nm) Films of Silicon", Appl. Phys. Lett. 44, 603 (1984).

T. Yonehara, Henry I. Smith, C.V. Thompson and J.E. Palmer, "Graphoepitaxy of Ge on SiO_2 by Solid-State Surface-Energy-Driven Grain Growth", Appl. Phys. Lett., 15 Sept. 1984.

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Conference Presentations (Abstract Only)

C.V. Thompson and H.I. Smith, "Silicon-on-Insulator by Solid State Surface-Energy-Driven Secondary Recrystallization", 1983 Electronic Materials Conference, Burlington, VT., June 1983.

H.I. Smith, "Graphoepitaxy to Circumvent Lattice Matching Constraints", presented at the Fourth International Conference on Integrated Optics and Optical Fiber Communication (Post-Conference Meeting), Tokyo, Japan, July 2, 1983. (Invited)

H.I. Smith, "Graphoepitaxy and Zone-Melting Recrystallization of Patterned Films", presented at the VII. International Conference on Crystal Growth, Stuttgart, FRG, September 12-16, 1983. (Invited)

C.V. Thompson and H.I. Smith, "Silicon-on-Insulator by Surface-Energy-Driven Secondary Recrystallization with Patterning", presented at the VII International Conference on Crystal Growth, Stuttgart, FRG, September 12-16, 1983.

T. Yonehara, Henry I. Smith, C.V. Thompson and J.E. Palmer, "Graphoepitaxy of Ge by Solid-State Surface-Energy-Driven Secondary Grain Growth", presented at Sixth American Conference on Crystal Growth and Sixth International Conference on Vapor Growth and Epitaxy, Atlantic City, NJ, July 15-20, 1984.

T. Yonehara, Henry I. Smith, C.V. Thompson and J.E. Palmer, "Surface-Energy-Driven Graphoepitaxy in Ultra-Thin Films of Ge", to be presented at 1984 International Conference on Solid State Devices and Materials, Kobe, Japan, August 30-Sept. 1, 1984.

Theses

S.S. Dana, "Nucleation on Surface Relief Structures by Chemical Vapor Deposition", Ph.D. Thesis, Department of Physics, Massachusetts Institute of Technology, September 1983.

E.H. Anderson, "Surface Gratings with Sub-100 nm Linewidths", M.S. Thesis, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, June 1984.

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